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VISCOSITY STUDIES OF SYSTEM
 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$: II, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$

BY
J. S. MACHIN AND TIN BOO YEE

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Topographic Mapping in Cooperation with the United States Geological Survey.

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VISCOSITY STUDIES OF SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$:

II, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$

BY

J. S. MACHIN AND TIN BOO YEE

ABSTRACT

Viscosity data are presented covering those compositions in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system which are liquid at 1500°C . The pattern of isokoms on the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ face of the compositional tetrahedron which represents the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system is a system of lines which roughly parallel the lines along which the lime content is constant. There are, however, considerable deviations from this parallelism in regions of very low and very high alumina content.

INTRODUCTION

The reasons for undertaking these studies were presented in the first paper of this series¹ where the apparatus and experimental techniques are described.

The field of compositions covered by the experiments on which the data presented in table I are based is roughly that bounded by the 1500°C . isotherm on the equilibrium diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ according to Schairer.² The compositional field investigated was covered at 5% intervals.

GRAPHIC TREATMENT OF VISCOSITY DATA

Values for the viscosity at points between the experimental points were obtained by interpolation in the following manner: The values for the viscosities of all compositions with a given silica content were plotted on a logarithmic scale as ordinates against the alumina content on a linear scale as abscissas. The curve was drawn through the points representing viscosities at the same temperature.

The process was repeated on separate plots, keeping other components constant and varying the silica. The compositions

corresponding to whole-number viscosities were read from the semilogarithmic curves and were plotted on the triaxial diagrams of figure 1. The best curve drawn through all of the points representing a constant viscosity at a given temperature was taken as the isokom (line of constant viscosity) for that temperature. Most of the plotted points lie within 0.2 compositional percent of the isokom. A few depart by as much as 0.5 or 0.6 compositional percent.

GENERAL TRENDS IN THE DATA

The isokoms are roughly parallel to the lines along which the molar acid-base ratios are constant. Alumina is considered to be acid in calculating this ratio. In the range of compositions under consideration the lines of constant lime composition are also roughly parallel to the constant acid-base ratio lines. The isokoms depart considerably from this parallelism in the region where the lime content is less than 25%.

The viscosity increases with increasing silica and with increasing alumina. The S-shaped isokoms show minimum change of viscosity with variation of alumina content near the ends. In the region of 60% and more silica, alumina appears to be less effective in increasing viscosity; this is also the case in the region of 40% and less silica. In the area between these limits the effect of alumina on the melt viscosity is nearly as great as that of silica.

¹J. S. Machin and D. L. Hanna, "Viscosity Studies of System $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$: I, 40% SiO_2 ," *J. Am. Ceram. Soc.*, 28 [11] 310-16 (1945); *Illinois State Geol. Survey Rept. Investigations*, No. 111 (1946).

²J. F. Schairer, "The System $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$: I, Results of Quenching Experiments on Five Joins," *J. Am. Ceram. Soc.*, 25 [10] 241-74 (June, 1942).

TABLE I.—VISCOSITY DATA
Lime-Magnesia-Alumina-Silica System (MgO = 0%)

| Melt No. | Composition (wt. %) | | | Viscosity (poises) at °C. | | | | | | | |
|----------|---------------------|-----|--------------------------------|---------------------------|------|--------|--------|---------|--------|---------|--------|
| | SiO ₂ | CaO | Al ₂ O ₃ | 1500 | 1450 | 1400 | 1350 | 1300 | 1250 | 1200 | 1150 |
| 1-146.5 | 30 | 35 | 35 | 10.2 | | | | | | | |
| 2-118R | 35 | 45 | 20 | 4.96 | 7.60 | 13.6 | | | | | |
| 3-141 | 35 | 40 | 25 | 7.53 | 11.9 | 19.9 | | | | | |
| 4-144R | 35 | 35 | 30 | 11.6 | 18.9 | 31.7 | | | | | |
| 5-146 | 35 | 30 | 35 | 19.0 | 31.4 | 54.7 | 109 | 248 | | | |
| 6-147 | 35 | 25 | 40 | 24.9 | 40.9 | | | | | | |
| 7-5 | 40 | 50 | 10 | 4.01 | 5.23 | 8.33 | | | | | |
| 8-11 | 40 | 45 | 15 | 5.16 | 8.22 | 13.2 | 22.2 | 40.3 | 85.8 | | |
| 9-17 | 40 | 40 | 20 | 8.32 | 13.7 | 21.5 | 35.1 | 67.6 | 148 | | |
| 10-22 | 40 | 35 | 25 | 14.3 | 21.7 | 34.9 | 63.9 | 128 | 283 | | |
| 11-25 | 40 | 30 | 30 | 27.1 | 39.5 | 69.4 | 129 | | | | |
| 12-54 | 45 | 55 | 0 | 2.33 | | | | | | | |
| 13-60 | 45 | 50 | 5 | 3.41 | 4.80 | | | | | | |
| 14-67 | 45 | 45 | 10 | 4.88 | 7.57 | 11.6 | | | | | |
| 15-73 | 45 | 40 | 15 | 8.54 | 12.5 | 19.4 | 33.1 | | | | |
| 16-79 | 45 | 35 | 20 | 15.0 | 22.6 | 37.1 | 63.3 | 125 | 272 | 674 | |
| 17-90 | 45 | 30 | 25 | 26.3 | 41.0 | 70.1 | 132 | | | | |
| 18-96 | 45 | 25 | 30 | 70.5 | | | | | | | |
| 19-131 | 50 | 45 | 5 | 4.78 | | | | | | | |
| 20-126R | 50 | 40 | 10 | 8.23 | 12.1 | 19.2 | | | | | |
| 21-121R | 50 | 35 | 15 | 14.3 | 21.9 | 34.7 | 57.1 | 105 | 209 | 469 | 1,250 |
| 22-117R | 50 | 30 | 20 | 30.2 | 42.3 | 70.9 | 125 | 247 | 529 | | |
| 23-140 | 50 | 25 | 25 | 57.7 | 99.8 | | | | | | |
| 24-130 | 55 | 40 | 5 | 8.40 | 12.8 | | | | | | |
| 25-125 | 55 | 35 | 10 | 15.1 | 22.3 | 35.7 | 60.8 | 117 | | | |
| 26-120 | 55 | 30 | 15 | 28.6 | 44.8 | 73.2 | 121 | 225 | 456 | 1,080 | 2,780 |
| 27-116 | 55 | 25 | 20 | 61.5 | 98.7 | 171 | 309 | 580 | 1,200 | 2,870 | 7,950 |
| 28-139 | 55 | 20 | 25 | 173 | 317 | 660 | | | | | |
| 29-134 | 60 | 40 | 0 | 9.23 | | | | | | | |
| 30-129 | 60 | 35 | 5 | 17.1 | 25.0 | 39.4 | | | | | |
| 31-124 | 60 | 30 | 10 | 32.6 | 51.7 | 81.6 | 126 | 220 | 421 | 990 | 2,520 |
| 32-119 | 60 | 25 | 15 | 77.7 | 128 | 214 | 391 | 730 | 1,560 | 3,730 | 10,600 |
| 33-115 | 60 | 20 | 20 | 204 | 353 | 663 | 1,260 | 2,530 | 5,750 | 14,700 | |
| 34-138 | 60 | 15 | 25 | 621 | 1220 | 2,500 | | | | | |
| 35-133 | 65 | 35 | 0 | 22.7 | | | | | | | |
| 36-128 | 65 | 30 | 5 | 42.2 | 69.9 | | | | | | |
| 37-123 | 65 | 25 | 10 | 94.6 | 152 | 256 | 460 | 854 | 1,780 | 4,160 | 11,100 |
| 38-114R | 65 | 20 | 15 | 311 | 574 | 1,040 | 1,960 | 4,500 | | | |
| 39-113 | 65 | 15 | 20 | 940 | 1590 | 3,210 | 6,440 | 14,700 | 31,200 | | |
| 40-112 | 65 | 10 | 25 | 1900 | 3960 | | | | | | |
| 41-123½ | 70 | 20 | 10 | 361 | 600 | 1,070 | | | | | |
| 42-114½ | 70 | 15 | 15 | 1320 | 2390 | 4,690 | 9,870 | 22,200 | 56,700 | 163,000 | |
| 43-113½ | 70 | 10 | 20 | 3950 | 8270 | 18,200 | 46,200 | 128,000 | | | |

DISCUSSION OF RESULTS

If alumina asserts its amphoteric character by behaving more and more as a basic component, as the acidity of the melt is increased by mounting silica, it might be expected that the isokoms in the high-silica region would bend in the direction opposite to that in which they actually do bend. In other words, alumina acting as a base would tend to reduce the number of oxygen bridges which bind silicon atoms together and so reduce the viscosity. In the low-silica region the bending of the isokoms is the more pronounced the greater the alumina content, and for the most part the bending is in the direction that might be expected if a part of the alumina were acting as a base, i.e., the viscosity is reduced. It appears, therefore, that the departure of the isokoms from straight lines in the high-silica region is probably not due to alumina playing a basic role. In the low-silica region this departure may be due to some such cause.

The lines along which R (the ratio of shared to unshared oxygen atoms¹) is constant intersect the isokoms at various angles ranging from 5° to more than 30° at points near the center of the isokoms. The angle is much greater near the ends of the S-shaped isokoms. This indicates that the simple theory proposed in the first paper of this series is insufficient.

Huggins³ has proposed a semiquantitative treatment based on thermodynamic calculations involving the energies of activation of breaking and making of silicon oxygen bonds in the chains and networks of atoms which are commonly considered to be the structural units of glass. At high temperatures the supply of thermal energy available is sufficient so that many units absorb enough to exceed that required to activate the break process; the structure, therefore, is continually changing within each small region. The viscosity is determined largely by the energy barriers which must be surmounted as the position of each small region is changed relative to neighboring regions.

These energy barriers must be made up of at least two types: (1) mechanical resistance or friction related to the size and configuration of the atom complexes which are the discrete units of the molten glass and (2) electrical potential energy barriers due to the charges which these complexes bear.

The system under consideration is further complicated by the fact that, in addition to silicon atoms, which are known to be capable of forming networks with the aid of oxygen bridges, it contains aluminum atoms which probably have the same capability, although in less degree.

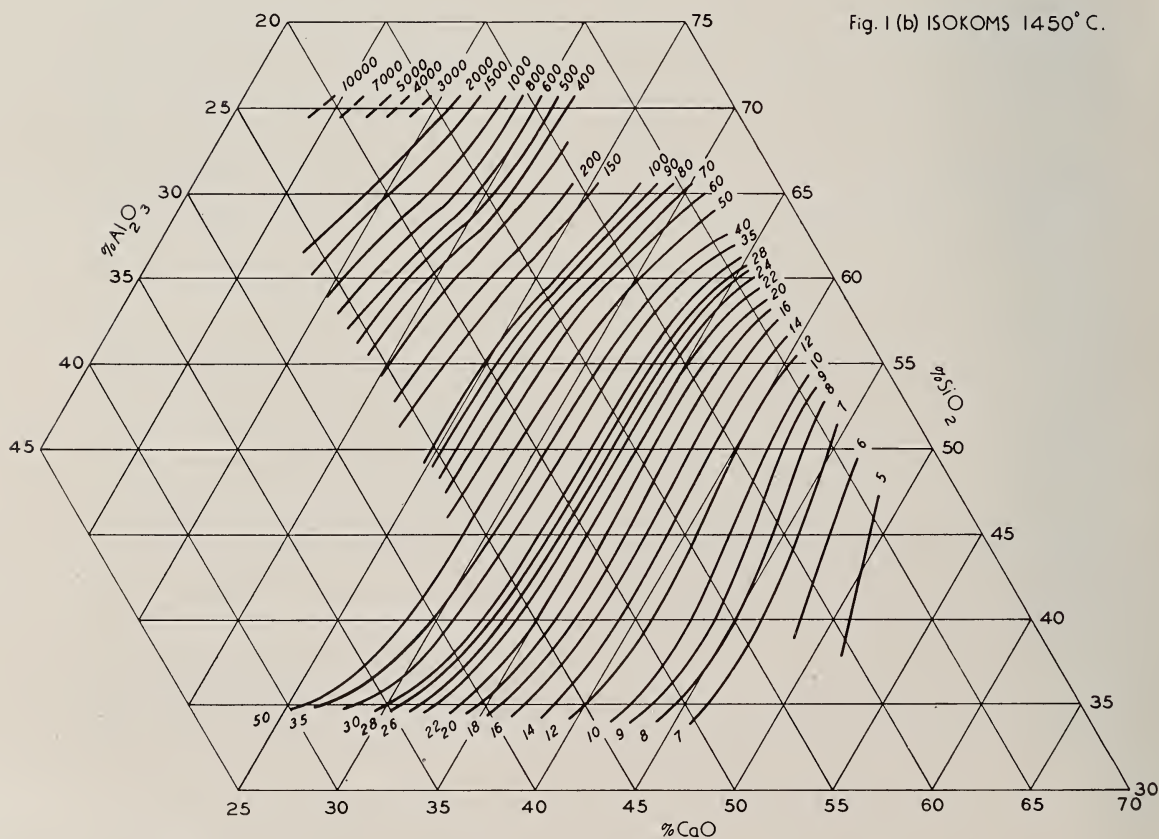
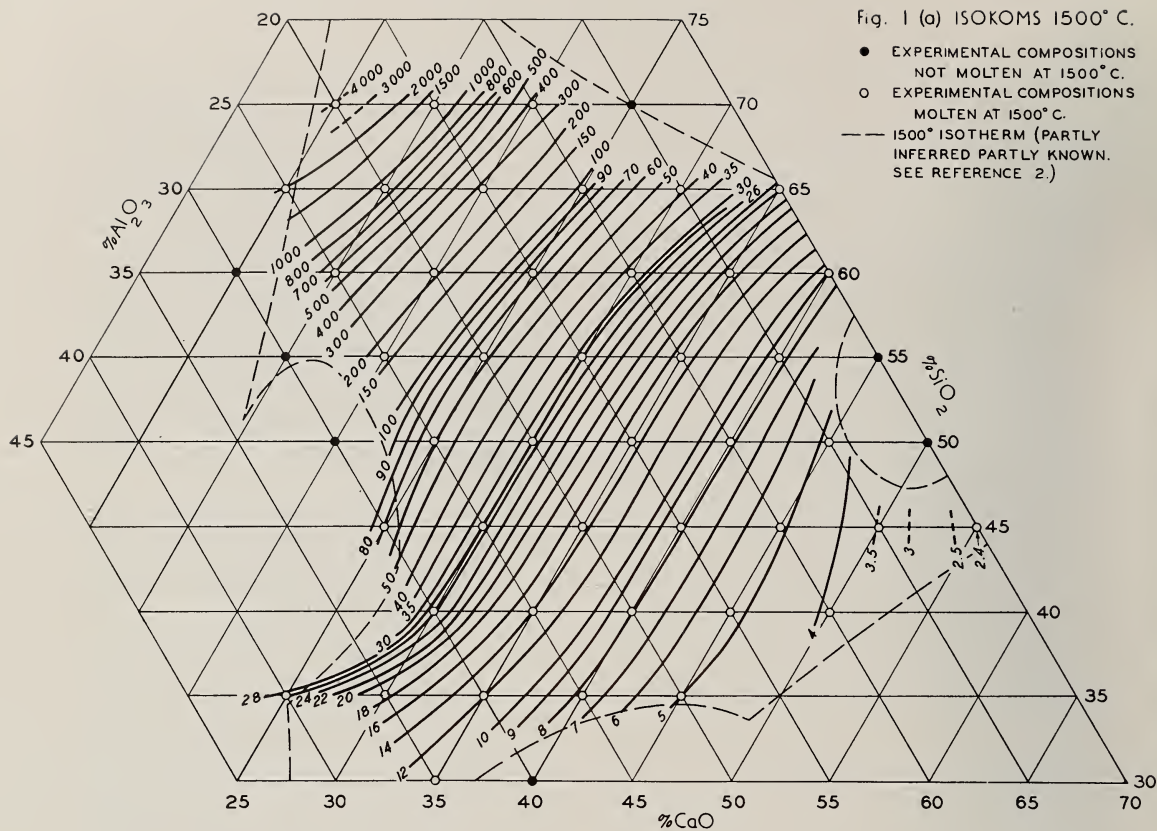
Sun⁴ has recently calculated the "bond strengths" of glass components. The viscosity of a melt is presumably largely determined by the proportion and size of large chainlike or network charged complexes present. In glasses these chains or networks are usually considered to be aggregates of positive atoms of valence greater than two, held together by oxygen atoms that are held in common by two of the positive atoms, e.g., silicon and aluminum. The strength of the bond between the oxygen and the positive atom might be expected to influence to a considerable degree the relative numbers of aggregates of various sizes present in the molten glass at a given temperature and hence also affect the viscosity. Sun's values for the energies of the oxygen-silicon and the oxygen-aluminum bonds are 106 and 79 (kilocalories per single Avogadro bond), respectively, for compounds containing both silicon and aluminum in addition to another metal, assuming that the coordination numbers of both silicon and aluminum are four. This seems to be a reasonable assumption since the compositional field under consideration is in large part identical with the crystallization fields of anorthite and gehlenite and includes the fields of no other aluminum silicates. The coordination number of aluminum has been reported to be four in both these compounds.⁵ If the coordination number of aluminum is six,

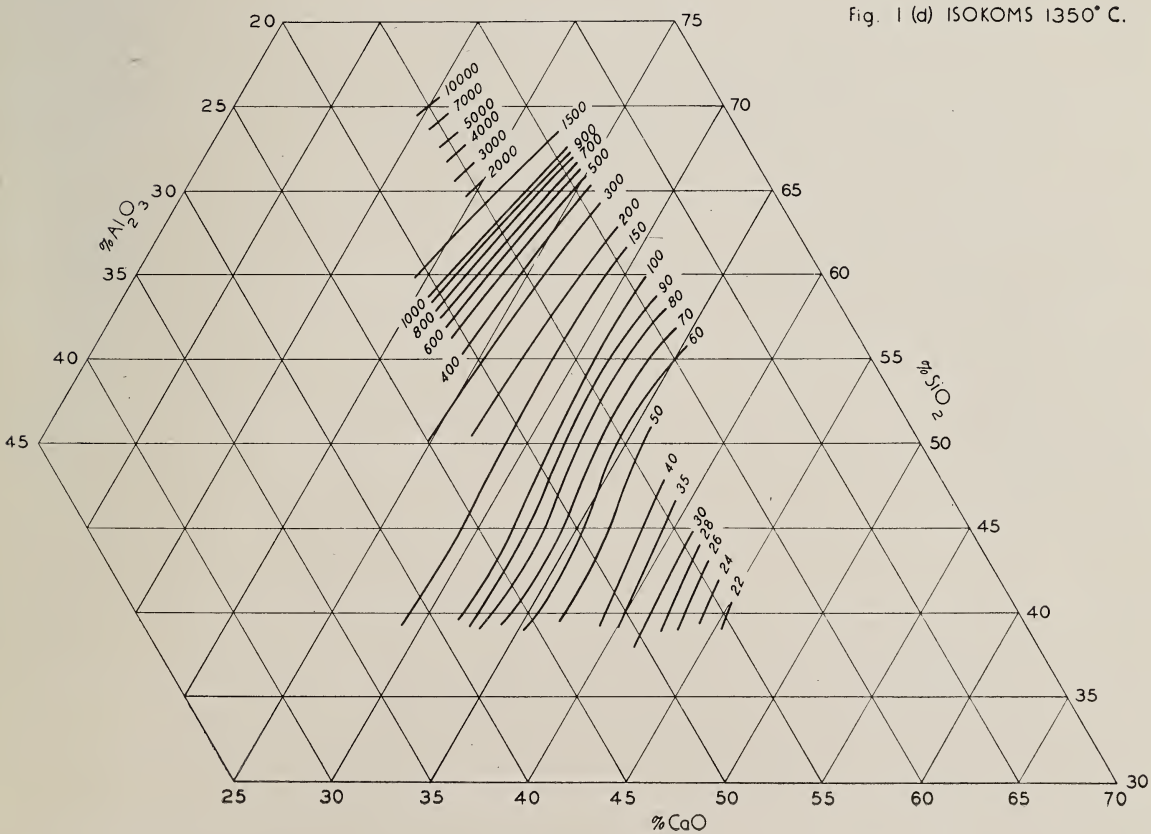
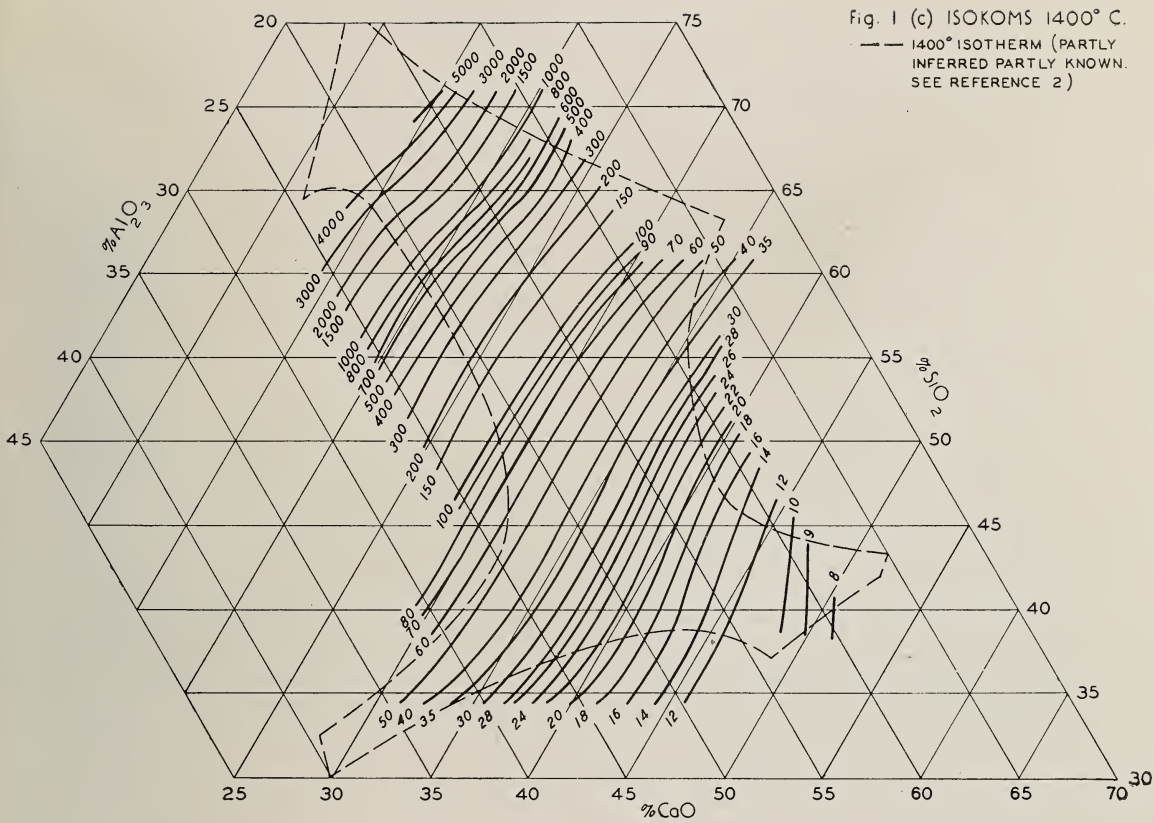
⁴K.-H. Sun, "Fundamental Condition of Glass Formation," *J. Am. Ceram. Soc.*, **30** [9] 277-81 (1947).

⁵(a) W. H. Taylor, J. A. Darbyshire, and H. Strunz, "An X-Ray Investigation of the Feldspars," *Z. Krist.*, **87** [6] 464-98 (1934); *Ceram. Abstracts*, **14** [4] 100 (1935).

(b) B. E. Warren, "The Structure of Melilite," *Z. Krist.*, **74** [2] 131-38 (1930); *Ceram. Abstracts*, **9** [11] 973 (1930).

³M. L. Huggins, "The Vitreous State: Some Semiquantitative Considerations," *J. Phys. Chem.*, **47**, 502-11 (1943); *Ceram. Abstracts*, **23** [6] 113 (1944).





the bond energy would drop to 53 for the oxygen-aluminum bond.

Calculation of the average bond energies (using Sun's figures) for compositions having the same silica content but varying alumina contents gives higher average bond energies for the lower alumina compositions than for the higher alumina compositions. The viscosity variation is in the reverse sense, indicating that the bond energy is not the unique critical factor in viscosity.

Figure 1 is comparable to figures 4 and 9 in a paper by McCaffery *et al.*⁶ The pattern of the isokoms in figure 1 is much simpler than that of McCaffery. In some regions of composition the agreement is quite good; in others there is definite disagreement. The disagreement is most pronounced in those regions which are contiguous to the 1500°

and the 1400° C. isotherms. In this study no evidence was found of the closed curves which McCaffery presents on either his 1500° diagram or his 1400° diagram.

It will be noted that McCaffery's 1500° and his 1400° diagrams cover considerably larger compositional areas than those presented here. This is not surprising in the case of the 1500° diagram because McCaffery started at 1600°C. It is not so apparent, however, why his melts should have undercooled over a considerable area of the 1400° diagram, which in this investigation showed definite evidence of crystallization or even complete solidification.

SUMMARY

The viscosities of compositions in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ which can be melted at 1500°C. and at lower temperatures have been measured. The data are presented in tabular and also in graphic form.

⁶R. S. McCaffery, J. F. Oesterle, and O. O. Fritsche, "Effect of Magnesia on Slag Viscosity" in "Viscosity of Blast-Furnace Slags," *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 383, 55-68 (1931); *Ceram. Abstracts*, 10 [6] 460 (1931).

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